

REPORT DOCUMENTATION PAGE				Form Approved OMB NO. 0704-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 22-09-2008		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1-Oct-2007 - 30-Jun-2008	
4. TITLE AND SUBTITLE Hierarchical Assemblies of Diblock Copolymer-Based Supramolecules In Thin Films				5a. CONTRACT NUMBER W911NF-07-1-0653	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 611102	
6. AUTHORS Ting Xu				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of California - Berkeley Sponsored Projects Office The Regents of the University of California Berkeley, CA 94704 -5940				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSOR/MONITOR'S ACRONYM(S) ARO	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) 53481-CH-II.1	
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT The hierarchical assemblies of supramolecules, consisted of polystyrene-b-poly(4-vinylpyridine) (PS-b-P4VP) with 3-pentadecylphenol (PDP) hydrogen-bonded to the 4VP, were investigated in thin films after solvent annealing in a chloroform atmosphere. The synergistic co-assembly of PS-b-P4VP and PDP was utilized to generate oriented hierarchical structures in thin films. Hierarchical assemblies, including lamellae-within-lamellae and cylinders-within-lamellae, were simultaneously ordered and oriented from a few to several tens of nanometers over macroscopic length scales. The macroscopic orientation of supramolecular assembly depends on the P4VP(PDP) fraction and can be tailored by varying the PDP to P4VP ratio					
15. SUBJECT TERMS Diblock Copolymer-based supramolecules, thin films, hierarchical assembly					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Ting Xu
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER 510-642-1632

## Report Title

### Hierarchical Assemblies of Diblock Copolymer-Based Supramolecules In Thin Films

#### ABSTRACT

The hierarchical assemblies of supramolecules, consisted of polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) with 3-pentadecylphenol (PDP) hydrogen-bonded to the 4VP, were investigated in thin films after solvent annealing in a chloroform atmosphere. The synergistic co-assembly of PS-*b*-P4VP and PDP was utilized to generate oriented hierarchical structures in thin films. Hierarchical assemblies, including lamellae-within-lamellae and cylinders-within-lamellae, were simultaneously ordered and oriented from a few to several tens of nanometers over macroscopic length scales. The macroscopic orientation of supramolecular assembly depends on the P4VP(PDP) fraction and can be tailored by varying the PDP to P4VP ratio without interfering with the supramolecular morphologies. The lamellar and cylindrical microdomains, with a periodicity of  $\sim 40$  nm, could be oriented normal to the surface, while the assembly of comb-blocks, P4VP(PDP), with a periodicity of  $\sim 4$  nm, were oriented parallel to the surface. Furthermore, using one PS-*b*-P4VP copolymer, thin films with different hierarchical structures, i.e. lamellae-within-lamellae and cylinders-within-lamellae, were obtained by varying the ratio of PDP to 4VP units. The concepts described in these studies can be potentially applied to other BCP-based supramolecular thin films, thus, creating an avenue to functional, hierarchically ordered thin films.

---

#### List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

##### (a) Papers published in peer-reviewed journals (N/A for none)

Tung, S.H., Kalarickal, N.C. & Xu, T. Hierarchical Assemblies of Diblock Copolymer-Based Supramolecules in Thin Films. *Macromolecules* 41, 6453-6462 (2008).

Number of Papers published in peer-reviewed journals: 1.00

---

##### (b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

---

##### (c) Presentations

Poster, American Physical Society, New Orleans, 2008

Number of Presentations: 1.00

---

##### Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

---

##### Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

---

##### (d) Manuscripts

Number of Manuscripts: 0.00

---

Number of Inventions:

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
N. C. . Kalarickal	0.30
Shih Huang Tung	0.50
FTE Equivalent:	0.80
Total Number:	2

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Ting Xu	0.08	No
FTE Equivalent:	0.08	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Cen Tan	1.00
FTE Equivalent:	1.00
Total Number:	1

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: .....	2.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	1.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	1.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....	3.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense .....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: .....	1.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

---

**Names of personnel receiving PhDs**

<u>NAME</u>
-------------

Total Number:
---------------

---

**Names of other research staff**

<u>NAME</u>
-------------

<u>PERCENT SUPPORTED</u>
--------------------------

FTE Equivalent:
-----------------

Total Number:
---------------

---

**Sub Contractors (DD882)**

**Inventions (DD882)**

## Report for the STIR program

### Project title:

Hierarchical Assemblies of Diblock Copolymer-Based Supramolecules in Thin films.

### Principle Investigator:

Ting Xu, Department of Materials Science and Engineering, Department of Chemistry, University of California, Berkeley

**Support period:** October 2007 – June 2008

**Support amount:** \$50,000

### Summary of achievement:

During this period, with the STIR support, we focused on the hierarchical assemblies of diblock copolymer-based supramolecules in thin films. Systematic studies were carried out to investigate the effect of a range of parameters, such as film thickness, sample treatment and sample composition, on the orientation of the supramolecular assemblies in thin films at two length scales, namely, tens of nanometers and a few nanometers; and how to achieve control over the macroscopic orientation in thin films. We showed that the macroscopic orientation of microdomains resulting from the block copolymer phase separation and the lamellar structures resulting from the assembly of comb block could be simultaneously controlled in thin films. During the process, we also made some very interesting observations. We pursued with two specific areas, namely to generate non-equilibrium nanostructures by selective removing the small molecules and to use small molecule to direct nanoparticle assemblies. We published one paper in *Macromolecules* and currently there are two manuscripts in preparation.<sup>1</sup> We are in the process of filing one patent.

Research supported through this STIR program also led to a project funded by the NSF-DMR and two awards for the PI (3M Nontenured Faculty Award and DuPont Young Professor Award)

### Detailed main achievements:

**Achievement 1.** The hierarchical assemblies of supramolecules, consisted of polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) with 3-pentadecylphenol (PDP) hydrogen-bonded to the 4VP, were investigated in thin films after solvent annealing in a chloroform atmosphere. The synergistic co-assembly of PS-*b*-P4VP and PDP was utilized to generate oriented hierarchical structures in thin films. Hierarchical assemblies, including lamellae-within-lamellae and cylinders-within-lamellae, were simultaneously ordered and oriented from a few to several tens of nanometers over macroscopic length scales. The macroscopic orientation of supramolecular assembly depends on the P4VP(PDP) fraction and can be tailored by varying the PDP to P4VP ratio without interfering with the supramolecular morphologies. The lamellar and cylindrical microdomains, with a periodicity of ~ 40 nm, could be oriented normal to the surface, while the assembly of comb-blocks, P4VP(PDP), with a periodicity of ~ 4 nm, were oriented parallel to the surface, as shown in Figure 1.1-3. Furthermore, using one PS-*b*-P4VP copolymer, thin films with different hierarchical structures, i.e. lamellae-within-lamellae and cylinders-

within-lamellae, were obtained by varying the ratio of PDP to 4VP units. The concepts described in these studies can be potentially applied to other BCP-based supramolecular thin films, thus, creating an avenue to functional, hierarchically ordered thin films.

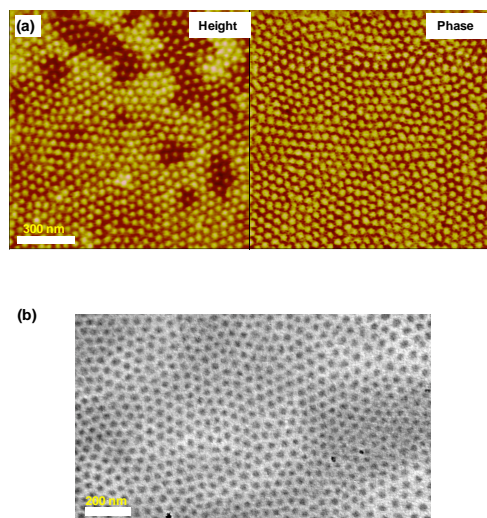


Figure 1.1 The (a) AFM and (b) TEM images of PS-b-P4VP(PDP) thin films. Cylindrical microdomains oriented normal to the surface can be clearly seen.

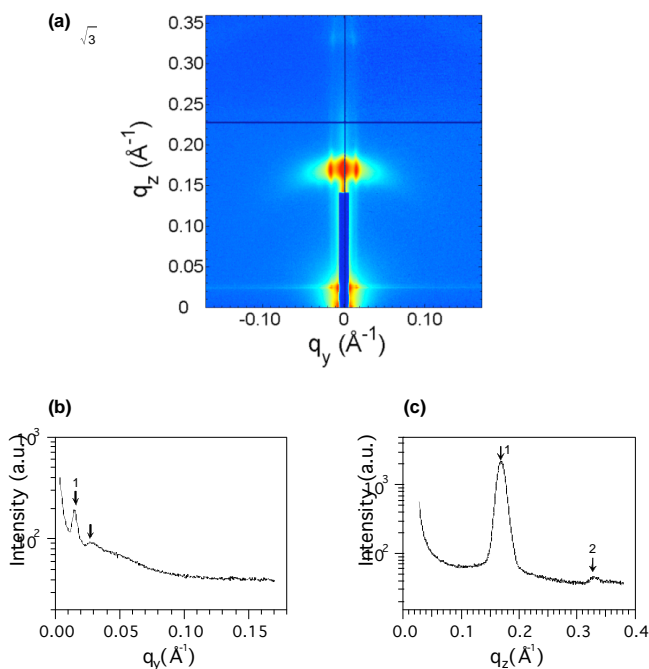


Figure 1.2 The grazing incidence small angle X-ray scattering (GISAXS) pattern of a  $\sim 49$  nm supramolecular thin film at an incident angle of  $0.2^\circ$ . (b) The  $q_y$  scan at  $q_z = 0.152 \text{ \AA}^{-1}$ , showing the PS-rich cylindrical microdomains, 41.9 nm in periodicity, are oriented perpendicular to the surface. (c) The  $q_z$  scan at  $q_y = 0.015 \text{ \AA}^{-1}$ , showing the P4VP(PDP) lamellae, 3.8 nm in periodicity, are oriented parallel to the surface. Both scans are extracted from the right side of the GISAXS pattern.

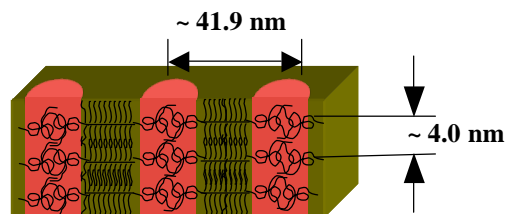


Figure 1.3 Schematic drawing of the lamellae-within-cylinder hierarchical structure in the supramolecular thin films.

**Achievement 2.** We developed a simple route to generate polygonal cylinders oriented normal to the surface in thin films using a combination of symmetric diblock copolymer and small molecules. Thin films with hexagonally packed circular cylinders oriented normal to the surface were first generated using a diblock copolymer-based supramolecules, consisted of symmetric polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) with 3-pentadecylphenol (PDP) hydrogen-bonded to the 4VP. After selective removal of ~90 % of the PDP, the films were solvent annealed under chloroform atmosphere for a short period of time (~ 3 hrs). Symmetric PS-*b*-P4VP containing a trace amount of PDP re-arranged within the structural frame initially formed by the PS-*b*-P4VP(PDP) supramolecules and assembled into polygonal cylindrical microdomains oriented normal to the surface, where most of the cross-sections of cylinders are hexagons as shown in Figure 2.1.

The reported route should be applicable to the large library of copolymer-based supramolecules reported previously. A large fraction of small molecules can be incorporated into the supramolecules without macrophase separation, the volume fraction of each block can be readily tailored to assess different morphologies using one block copolymer. Once the supramolecule assembled and upon selective removal of small molecules, the block copolymer will reassemble within a defined frame. This may not only lead to non-equilibrium nanostructures not readily accessible otherwise, but also enable fundamental studies on the pathway-dependent non-equilibrium structures in polymer thin films.

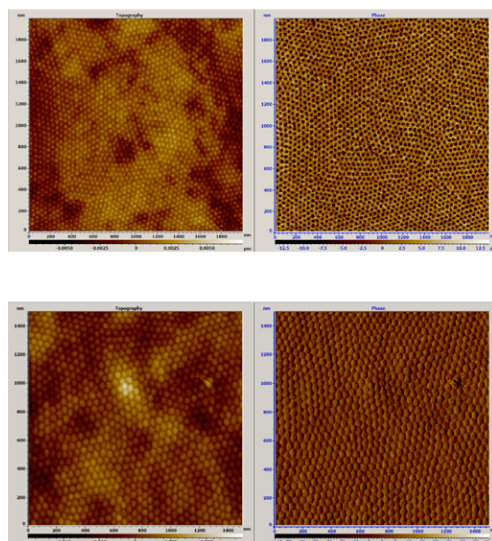


Figure 2.1 (Top) The AFM image of supramolecule thin films after solvent annealing. Hexagonally packed cylinder oriented normal to the surface can be clearly seen. (Bottom) The AFM image of the hexagonally packed polygons

3. We present results on the use of a diblock copolymer-based supramolecule to direct the assembly of cadmium selenide (CdSe) nanoparticles. The supramolecules were generated by hydrogen-bonding 3-pentadecylphenol (PDP) to the poly(4-vinyl pyridine) (P4VP) block of a diblock copolymer, poly(styrene-*b*-4-vinylpyridine) (PS-*b*-P4VP). The PS-*b*-P4VP(PDP) supramolecule forms a lamellae-within-lamellae hierarchical morphology. Transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS) studies (Figure 3.1) showed that the CdSe nanoparticles were homogeneously dispersed in the P4VP(PDP) lamellar microdomains of the PS-*b*-P4VP(PDP) supramolecule. The preferential interactions between the octadecylphosphonic acid (ODPA) ligands on the CdSe nanoparticles and the PDP provide a strong enthalpic driving force to incorporate CdSe nanoparticle within the P4VP(PDP) lamellar microdomains. The nanoparticles are arranged in a highly linear fashion within the lamellae morphologies with no detectable aggregation of the nanoparticles. To the best of our knowledge, this is the first attempt to use a combination of small molecules and diblock copolymers to direct the assembly of nanoparticle. The reported approach is simple and requires no surface chemistry of the nanoparticles or precise control over the nanoparticle size. Since the small molecules are not covalently linked and can be readily substituted, the reported approach.

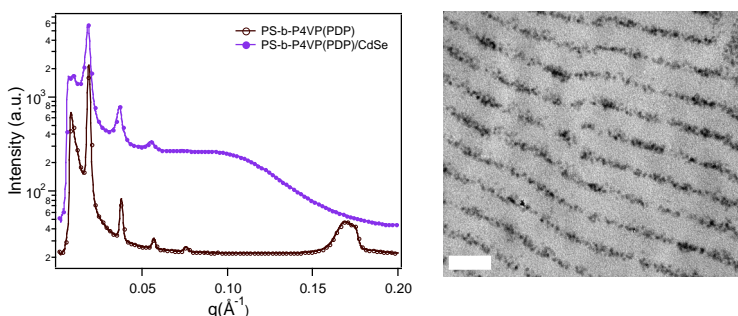


Figure 3.1 (Left) SAXS profiles of PS-*b*-P4VP(PDP) supramolecule and CdSe/PS-*b*-P4VP(PDP) blend with 9.2 wt % of  $\sim 4$  nm CdSe; (Right) TEM image of CdSe/PS-*b*-P4VP(PDP) blend with 9.2 wt % of CdSe. Scale bar: 50 nm.

#### Reference:

1. Tung, S.H., Kalarickal, N.C. & Xu, T. Hierarchical Assemblies of Diblock Copolymer-Based Supramolecules in Thin Films. *Macromolecules* **41**, 6453-6462 (2008).